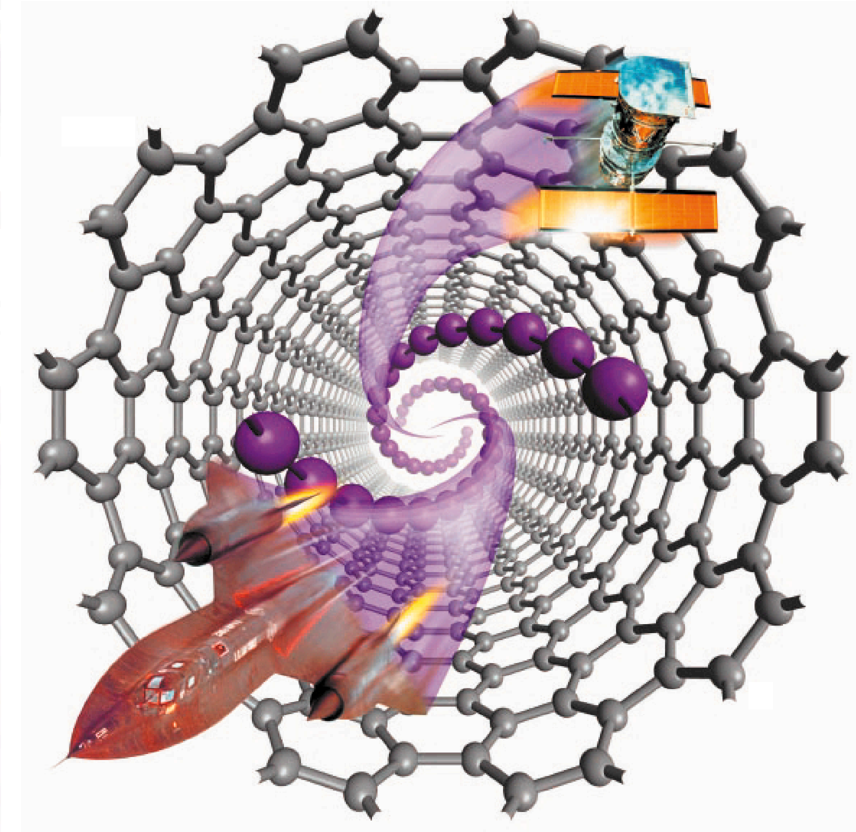
Functional Nanomaterials - *Advanced Synthesis and Processing of Carbon Nanotubes and their Composites*

PI's: David B. Geohegan
Alex A. Puretzky*
Ilia N. Ivanov*
Zhengwei Pan*
Philip F. Britt
CMSD and CSD, ORNL
**Mat. Sci. & Eng. Dept., Univ. of Tennessee*

Collaborators:
Apparao Rao *(Clemson Univ.)*
Tobias Hertel *(Vanderbilt Univ.)*
Graciela Blanchet *(DuPont Corp.)*
Michael Smith *(NASA Langley)*
Gyula Eres, H. Cui, J. Howe,
H.M. Christen, C.M. Rouleau



OAK RIDGE NATIONAL LABORATORY
Laboratory Directed Research and Development

OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY

CNMS Center for Nanophase Materials Sciences

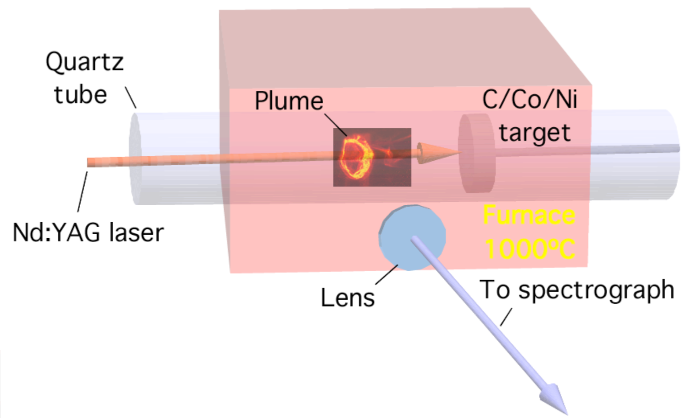
Functional Nanomaterials

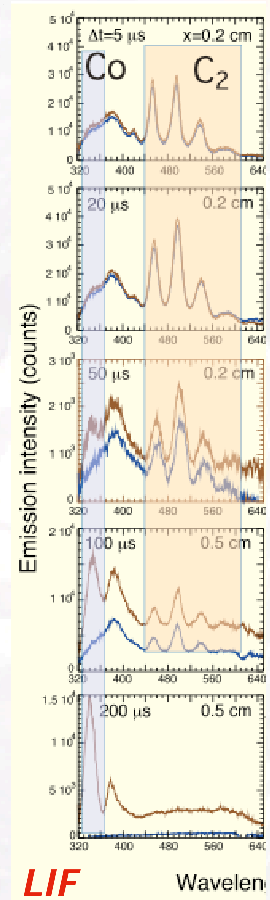
- **Unique ORNL Capabilities**
  - **Controlled synthesis of nanomaterials by PLV and CVD**
    - **In situ diagnostics, ex situ characterization**

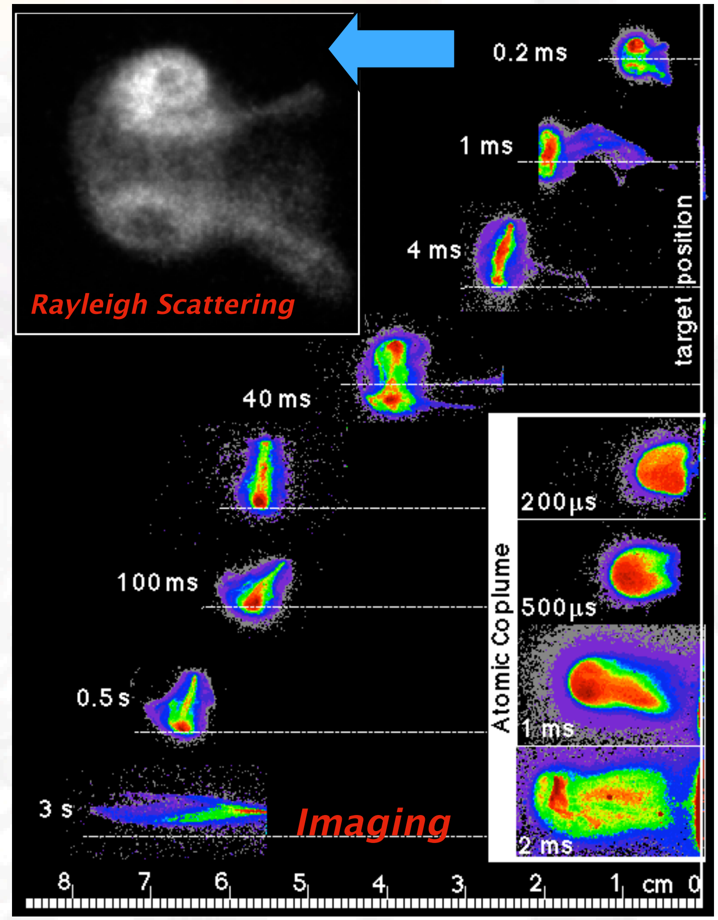
- **Recent Highlights at ORNL**
  - **First kinetics measurements of nanotube growth by CVD**
  - **Controlling nanotube lengths using in situ monitoring**
  - **Imaging functional nanotube networks in polymers**

- **Related User Proposals**
  - **Synthesis - Nanotube production at high rates - *NASA***
  - **Characterization - Combined electronic/imaging of nanotube transport for plastic electronics - *DuPont***
  - **Controlling doping in SWNTs - *Clemson***
  - **Charge carrier dynamics in size-selected SWNTs - *Vanderbilt***

SWNT Growth by Laser Vaporization – *In situ diagnostics facility*

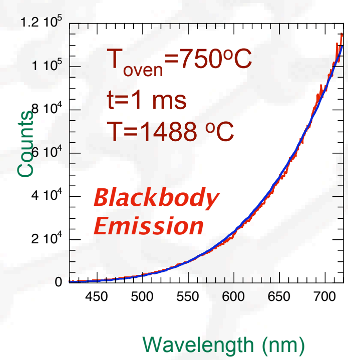


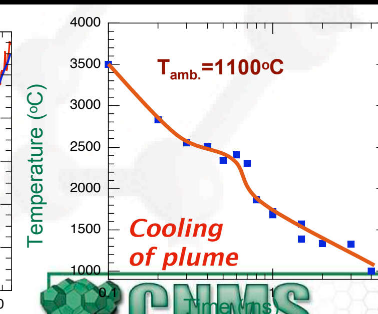




- First imaging of plume dynamics and spectroscopy of plume at extended times
  - First growth rates measured (1 – 5 µm/s)
  - Mechanism of growth deduced

- Position and dynamics
  - Gated ICCD imaging using 2nd laser
- Composition of the plume
  - Laser-induced fluorescence spectroscopy
- Temperature vs. time
  - Blackbody emission
  - Laser-induced incandescence
- Particle sizes
  - Rayleigh scattering
  - Optical absorption spectroscopy

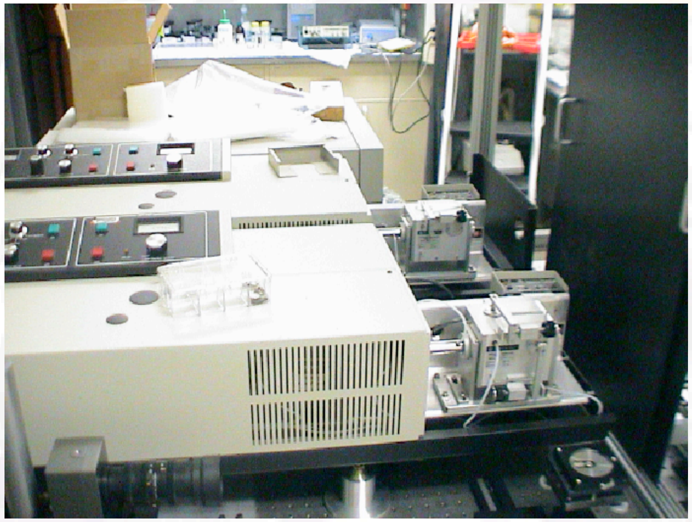




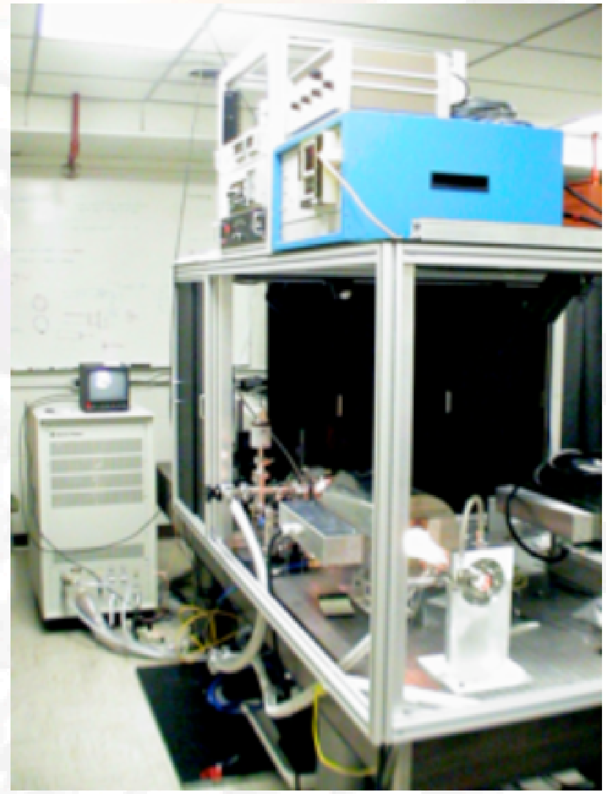
Appl. Phys. Lett. **76**, 182 (2000). *Appl. Phys. A* **70**, 153 (2000).
Appl. Phys. Lett. **78**, 3307-3309 (2001). *Phys. Rev. B* **65**, 245525 (2002).

Laser-Vaporization Production of SWNT at ORNL

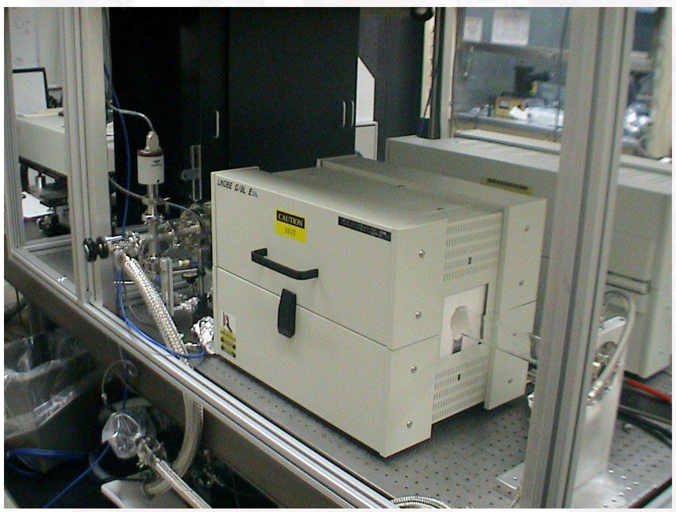
- Two pulsed Nd:YAG lasers
  - 30 Hz
  - 0.6 J/pulse
- Two 1200 ºC ovens
- ~ 1 gram/ 5 hours raw product
  - Up to 50-70 wt.% SWNT
- Automated beam scanning



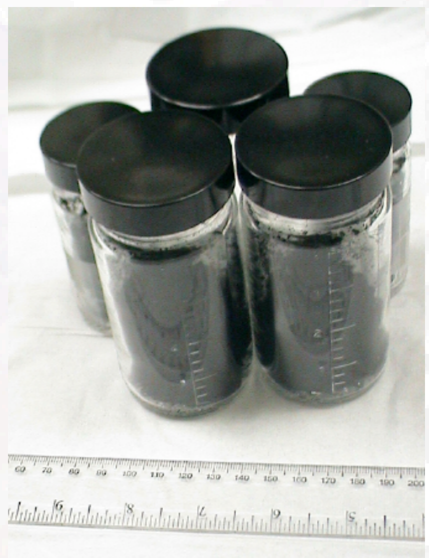
DCR-11 Nd:YAG lasers @ 1.06 μm



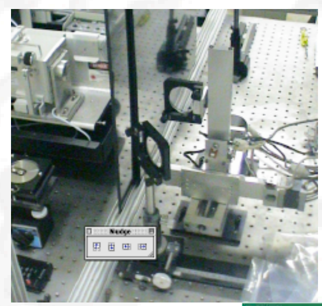
Setup overview



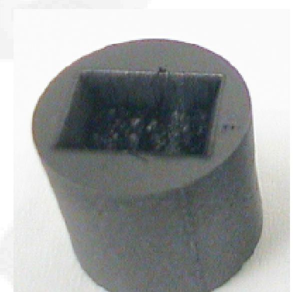
Pressure-controlled oven setup



1 gram SWNT / run



Beam scanner



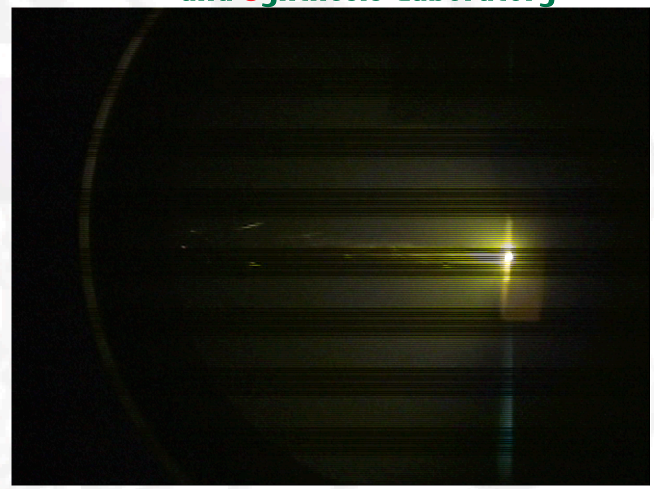
pellet

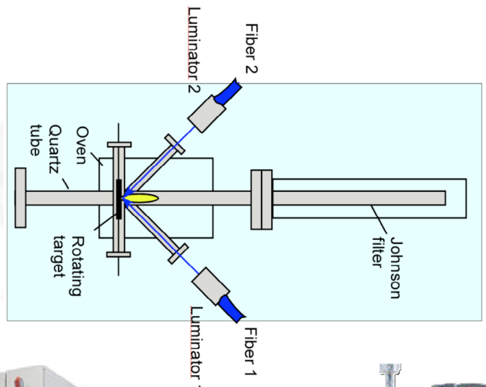
High-Power Laser Vaporization Nanomaterial Synthesis Facility

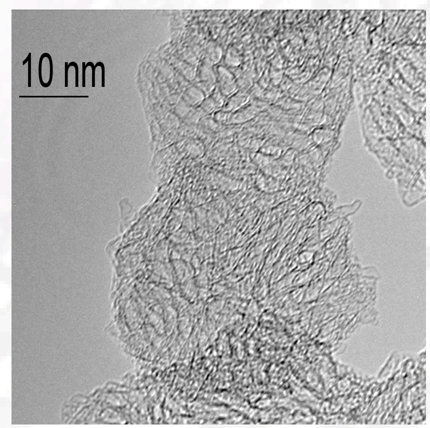
ALPS

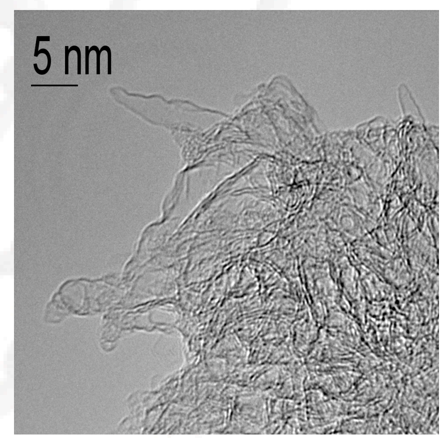
Advanced Laser Processing and Synthesis Laboratory

- Implementing an industrial laser to generate SWNT 10-30X faster than currently
- Extremely versatile - 600 W, 1.06 micron
- Also used for:
  - generation of SWNH, nanoparticles, and nanowires
  - Rapid IR heating in CVD growth









OAK RIDGE NATIONAL LABORATORY
U.S. DEPARTMENT OF ENERGY

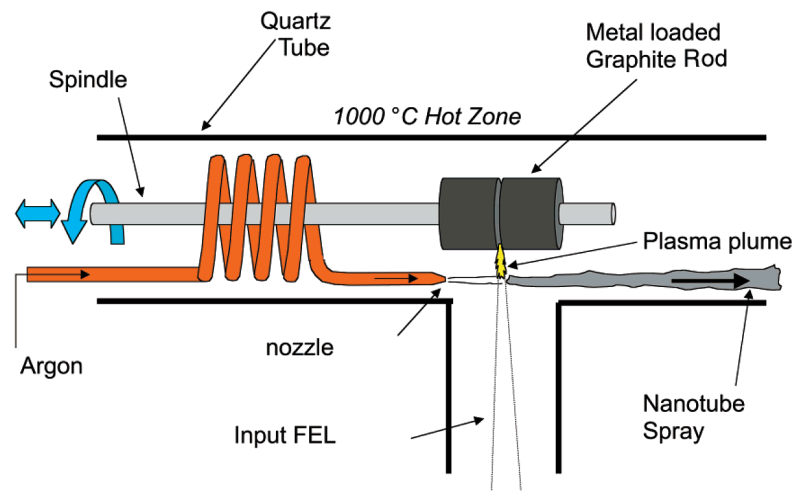
CNMS
Oak Ridge National Laboratory
Center for Nanophase Materials Sciences

CNMS 2003-050: M.W. Smith (NASA Langley)

Large-Scale Production of SWNTs using Ultrafast Pulses from a Free Electron Laser

- Can SWNTs be produced in high yields, at rapid growth rates with optimized ablation conditions?
- A comparison of laser pulse width (thermal vs. "nonthermal" ablation)
- FEL at JLAB (75 MHz, 50 fs, 1 kW)
- Novel flow reactor
- Continuous production, high yield

- We are co-designing optimized ablation geometry reactor to understand growth rates and the effect of pulse width on yield.



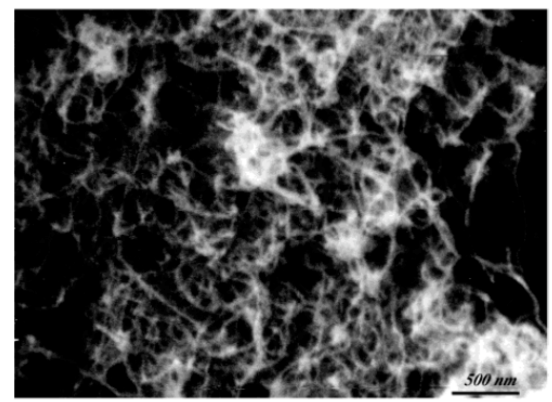
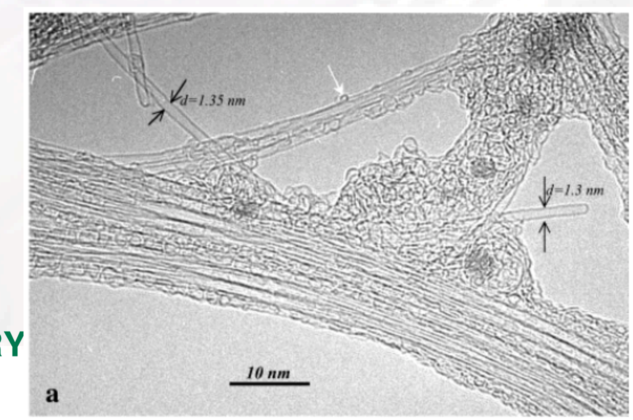
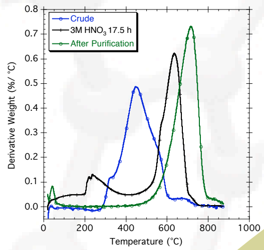


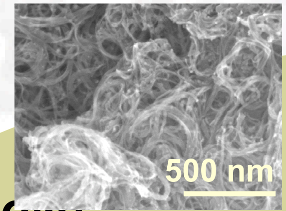
Figure 3. Scanning Electron Microscope (SEM) images of bundles of "as-prepared" SWNTs produced with Ni/Y (1.0 at. %/4.0 at. %).



SWNT Synthesis and Processing of Ultrahigh Purity SWNTs at ORNL - *Unique Expertise*



TGA



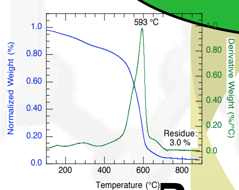
Raw Material

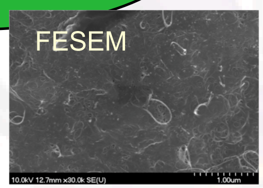
SEM, Raman, TGA

Targeted for Specific Applications

Remove Metal

Acid Etched



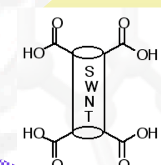


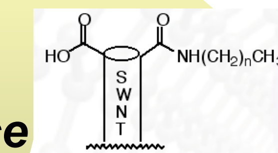
Remove a-C

Purification parameters optimized

- ***Acid reflux time***
- ***Acid concentration***
- ***Oxidation time***
- ***Physical separations***
- ***Additional oxidants***

Functionalization

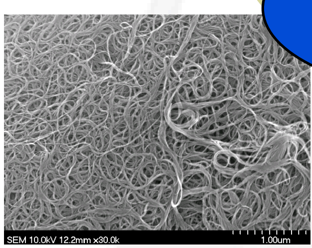


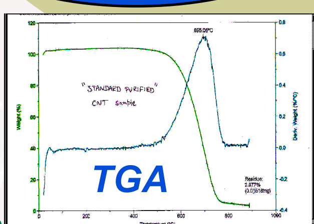


Replace Carboxyl Groups

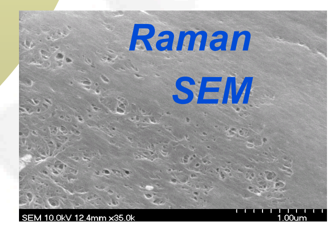
SEM, Raman

Oxidized



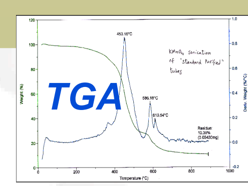


Processing



Defect Generation and Carboxylation

- ***Beam techniques***
- ***Sonication***
- ***Oxidation***

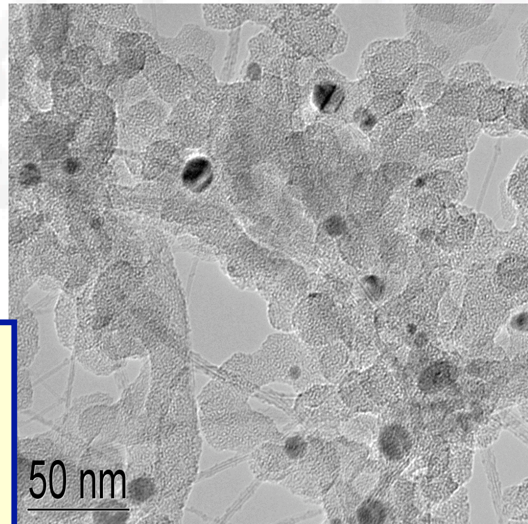


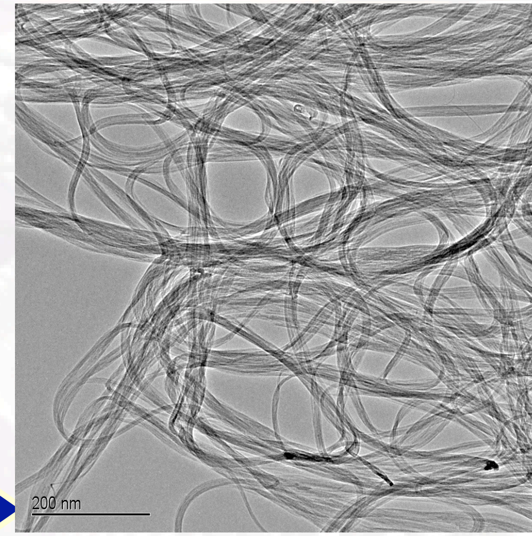
Highlight

Ultrahigh Purity SWNTs

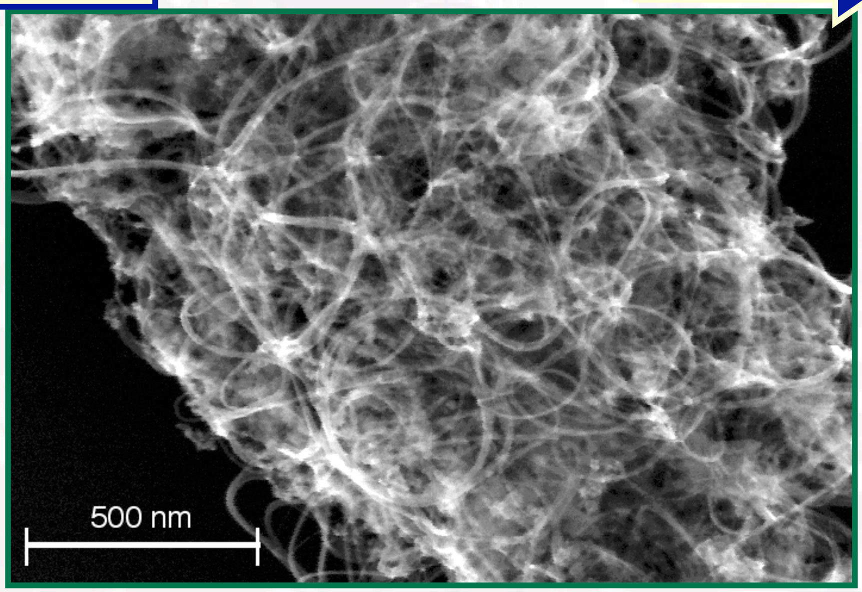
an essential starting point for nanotube chemistry

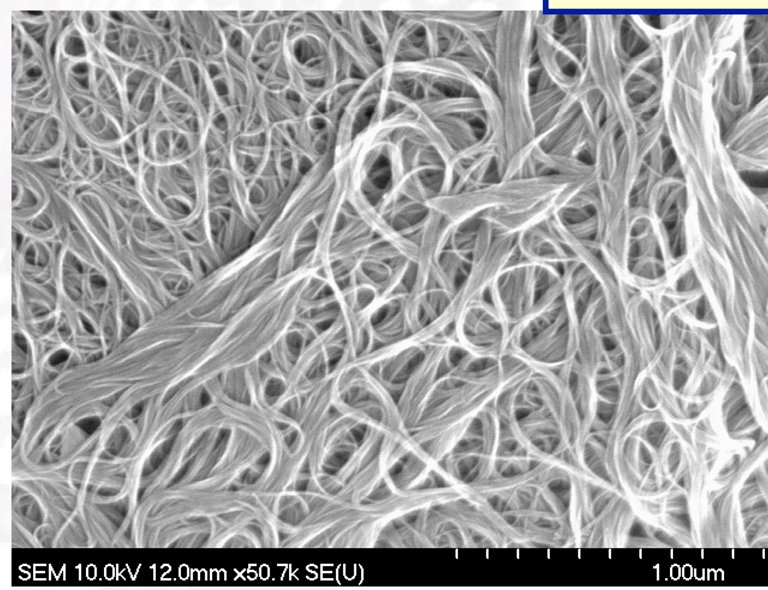
Raw Material
~ 50 wt. % SWNT





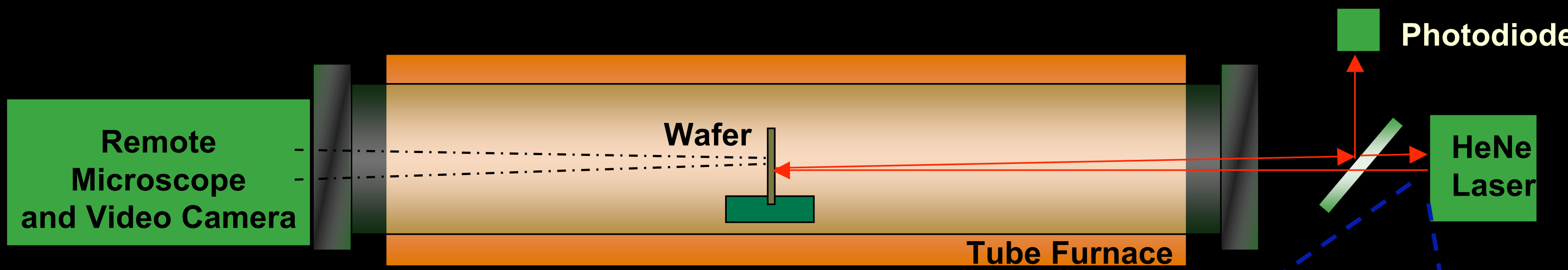
Purified Material
99.9+ wt. % SWNT

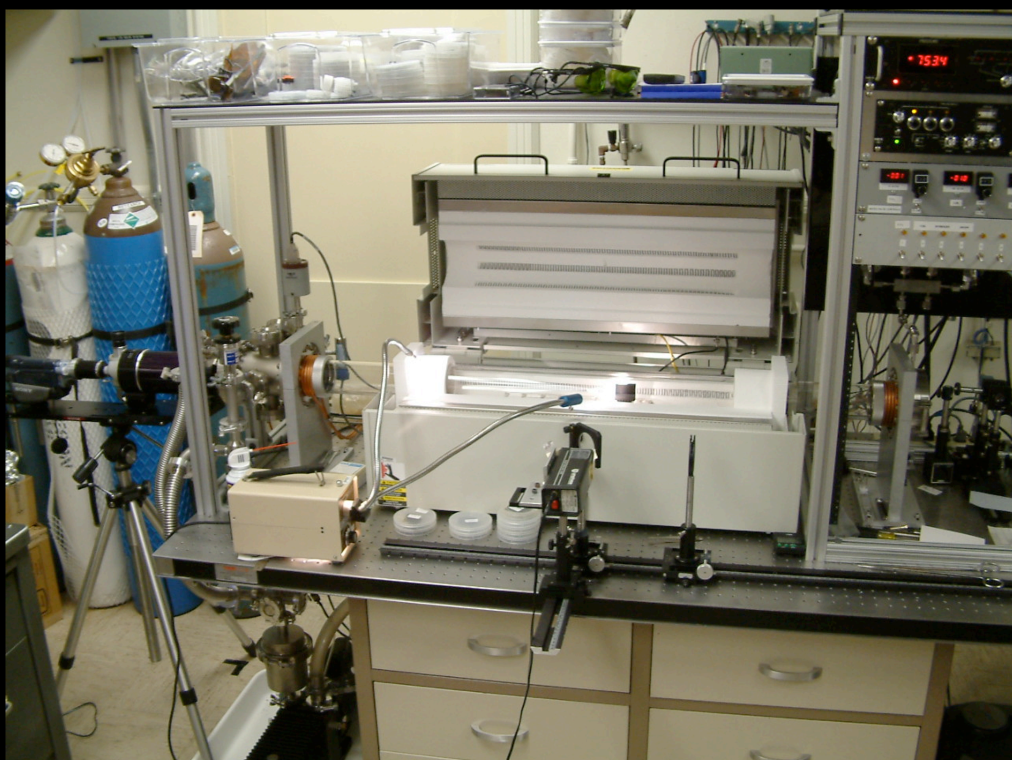


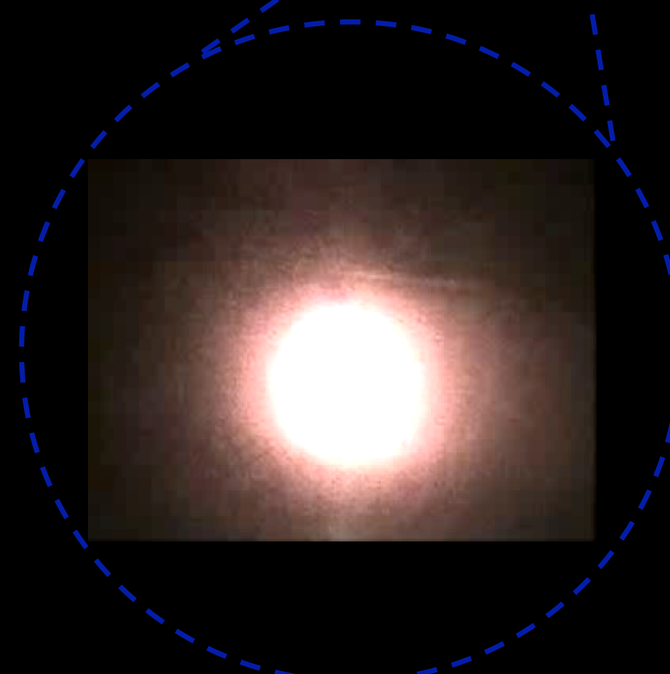


Growth of vertically-aligned nanotube arrays by CVD

In situ laser-interferometry, irradiation, and imaging during CVD



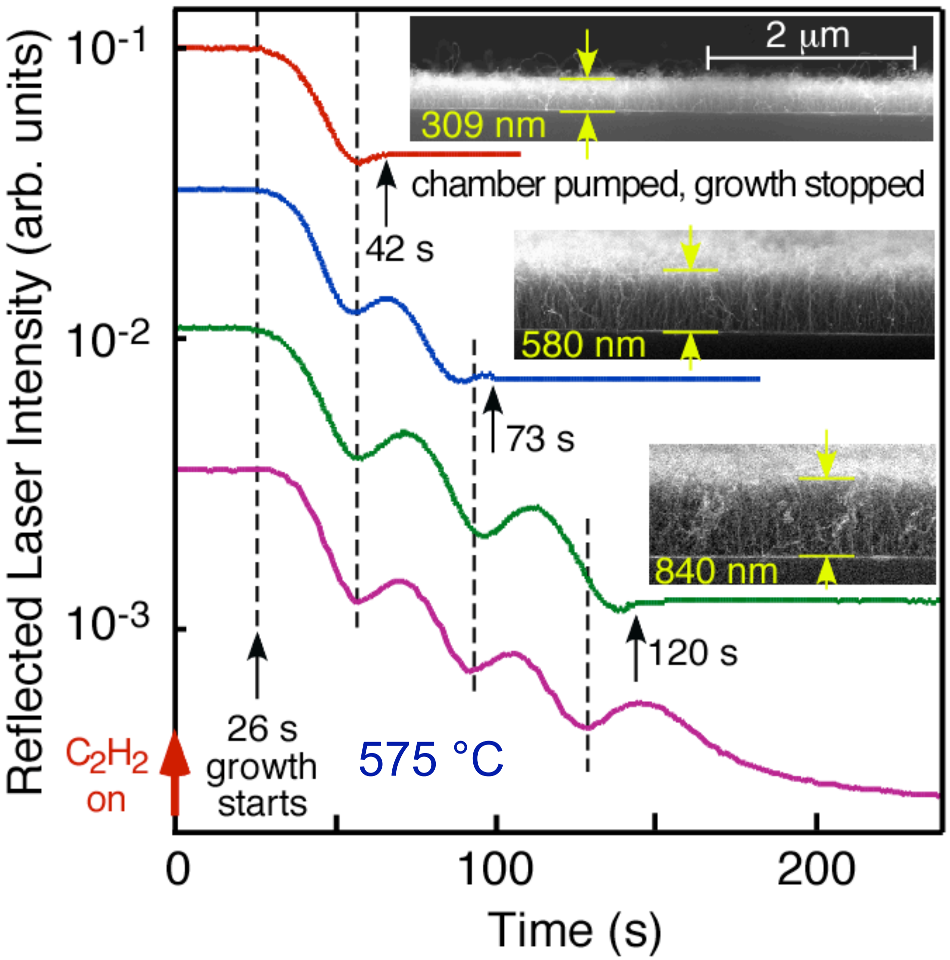




Reflected Spot

D. B. Geohegan, A. A. Puretzky, I. N. Ivanov, S. Jesse, G. Eres, and J. Y. Howe, Appl. Phys. Lett. **83**, *1851 (2003)*

Controlling the length of VAA-MWNT



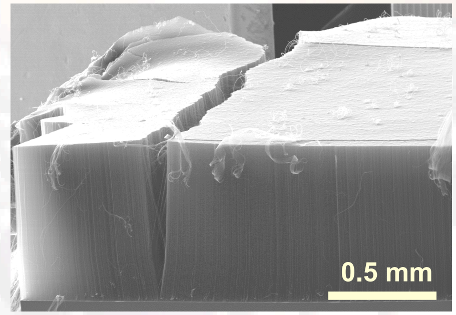
- Reflectivity can be used to monitor *and control* the length of vertically-aligned nanotube arrays
- Rapid evacuation of growth gas at predetermined lengths
- Can see growth stop.

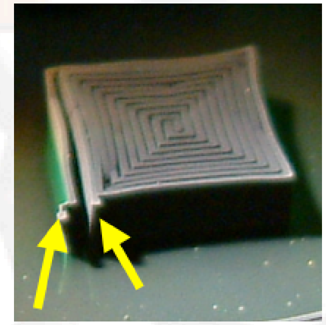
D. B. Geohegan, et al. Appl. Phys. Lett. **83**, *1851 (2003)*

CVD Growth of Vertically-Aligned Arrays of Carbon Nanotubes

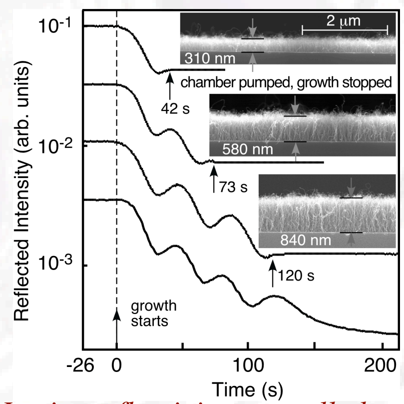
- **Vertically-aligned multiwall carbon nanotubes (VA-MWNT) grown by CVD over large areas – or *selectively* grown on lithographically-patterned catalyst films**
  - **Controlled growth to precise lengths with *in situ* diagnostics (in the nanometers to microns regime)**
  - **Alignment achieved for large diameter multiwalled nanotubes (MWNT) down to single-walled nanotubes (SWNT)**
  - **Rapid growth to millimeters lengths**
    - **Permits tensile, electrical conductivity, thermal conductivity tests on long, continuous fibers**

- **Infiltration of VA-MWNT with polymers for composites**
  - **Methods developed to preserve alignment**
  - **Young's modulus significantly enhanced**
  - **Increased oxidative thermal stability**
  - **Electrical conductivity in 3D, dissipates static charge**
  - **Enhanced thermal conductivity**
  - **Embedded sensor structures**
  - **Optically reflective coatings, optical filters**

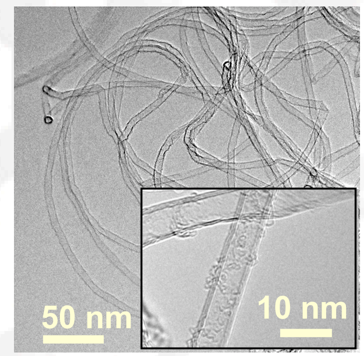




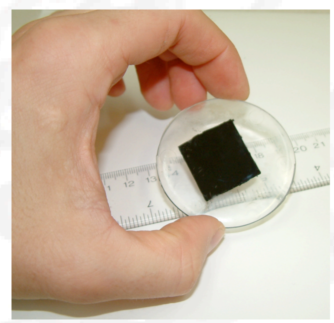
Macroscopic growth over large areas, or selective patterns

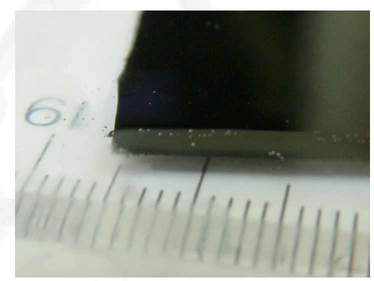


In situ reflectivity controlled-growth



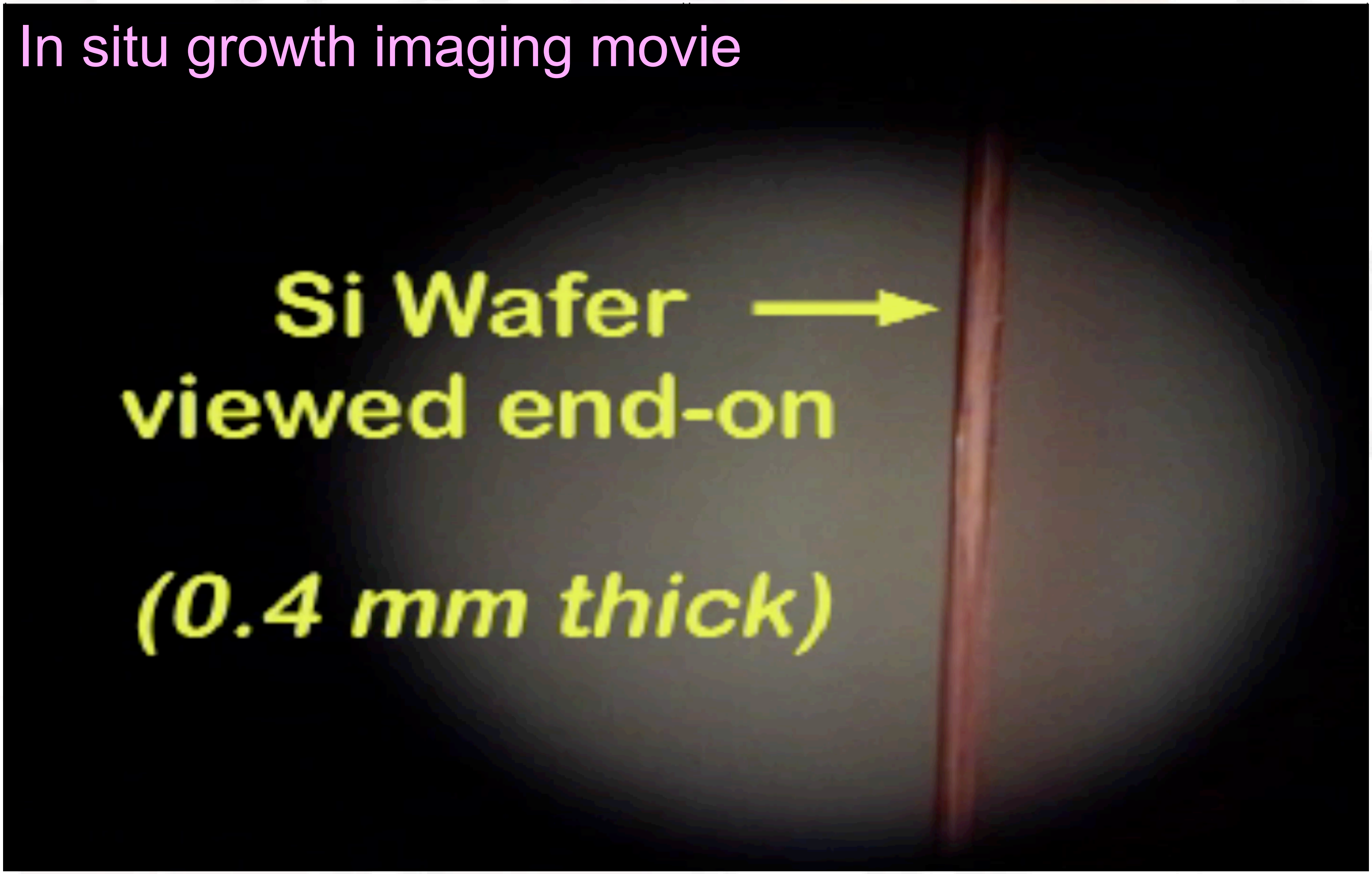
HRTEM of DWNT



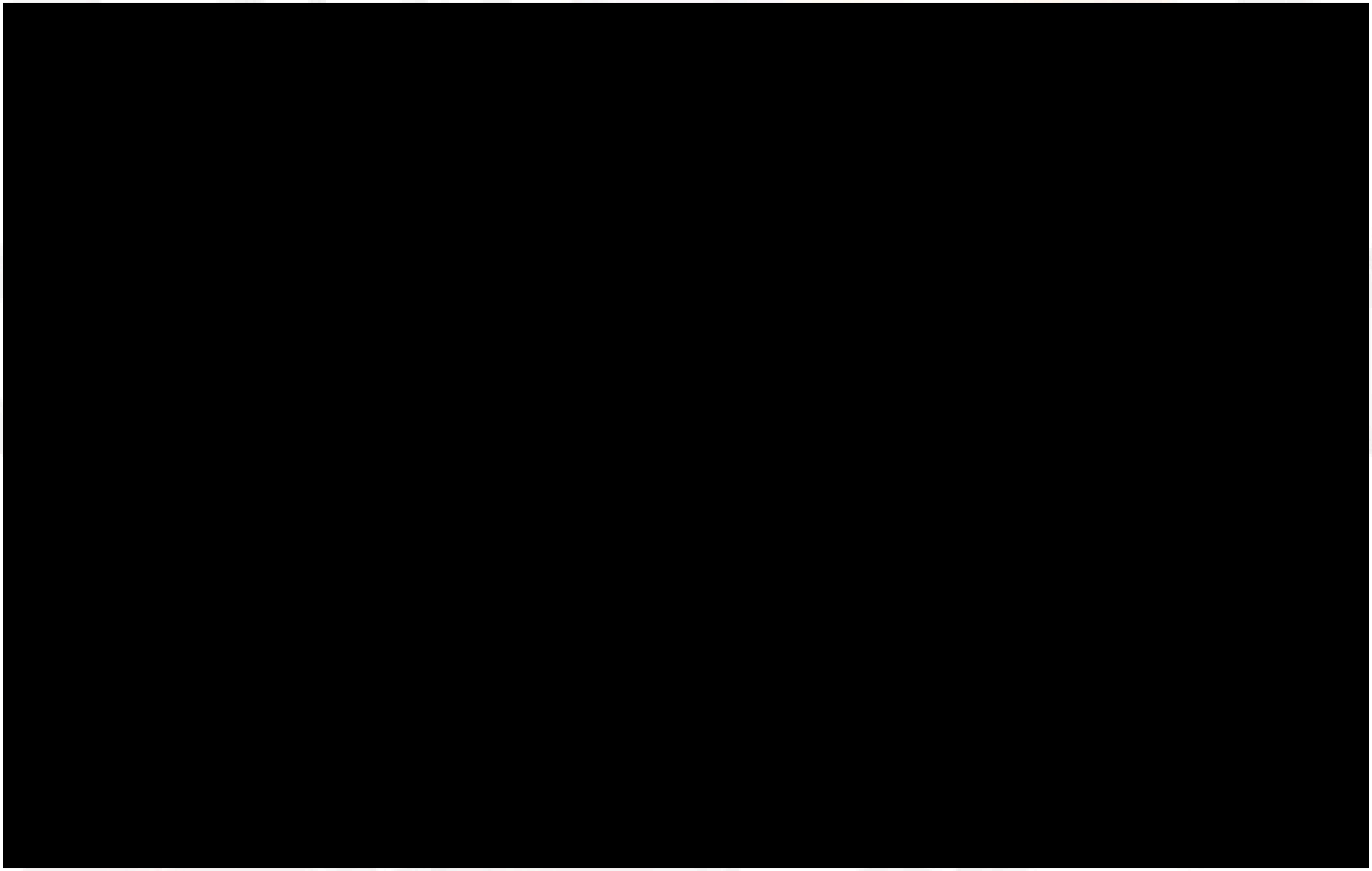


2 mm VA-MWNT in epoxy

Rapid Nanotube Array Growth to Millimeter Length

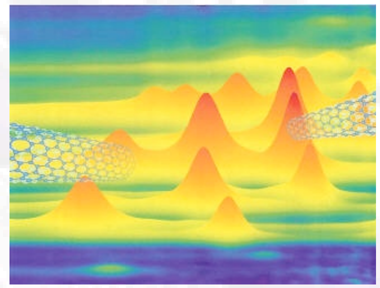


In situ kinetics measurements of CVD Nanotube Growth

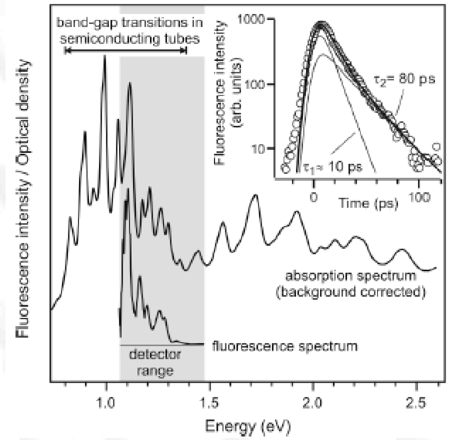


CNMS 2003-062: Tobias Hertel (Vanderbilt Univ.)
Charge-carrier dynamics and relaxation in optically excited SWNTs

- **Motivation**: SWNTs have discrete optical absorption and fluorescence bands
- **Why are quantum yields so low ($<10^{-3}$) ?**
- **Competition between radiative and non-radiative processes**



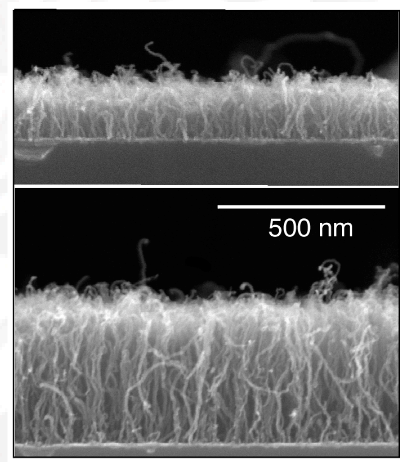
Distinct fluorescence peaks from different chiralities of SWNTs (courtesy of R.E. Smalley)



Absorption and fluorescent spectra of SWNTs, and (inset) time resolved fluorescence signal

- **Experiment**: Prepare well-characterized SWNTs (lengths, defect densities), dispersed in solution, and measure their charge carrier relaxation processes via fast fluorescence and photoemission measurements.

- **Challenge**: Grow SWNTs of different lengths, then harvest them and disperse them in solution.
  - How can length be controlled?



SEM images of VAA-MWNTs

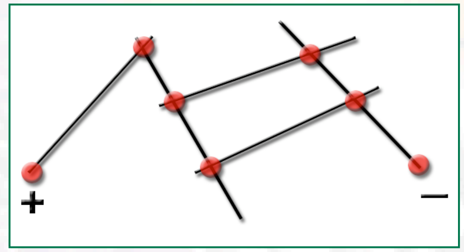
CNMS 2003-010: G. Blanchet (DuPont Corp.)
Tailoring Electronic Properties of Polyaniline/SWNT Composites

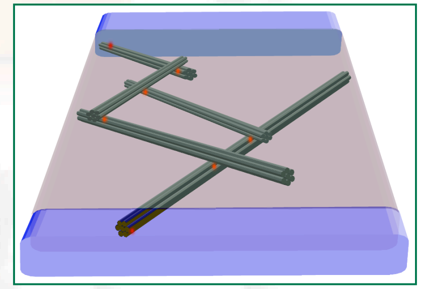
- Plastic Electronics
  - For organic large-area flexible displays, low-cost memory, disposable or wearable electronics
  - Polyaniline - A printable, environmentally-stable, conducting polymer with reversible conductivity depending upon doping, for plastic substrates
  - SWNT/ PANI composites become highly conductive (3 S/cm) at extremely low nanotube concentrations
    - 4 orders of magnitude improvement
    - PANi/SWNT devices outperfom devices with Au electrodes

- How does nanotube orientation affect carrier injection in PANi/SWNT composites?
  - Need to examine the morphology of the nanotube network inside the polymer and relate it to conduction
  - Need to understand if SWNT induce charge transfer at the SWNT/PANi interface or at the SWNT/PANi/semiconductor interface
- Will use and help develop new SEM imaging and I-V tools developed at ORNL

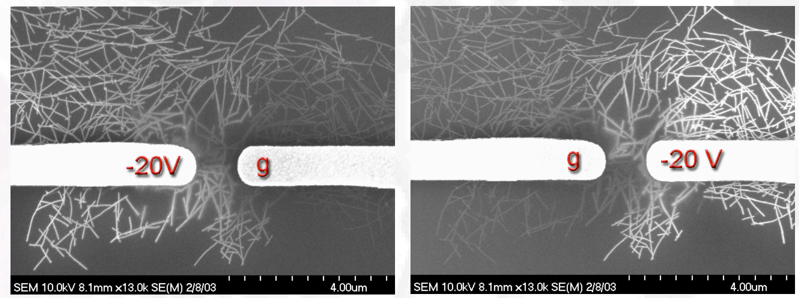
Imaging and Alignment of SWNT Networks in Polymers

- <u>Crosscutting Research Tasks</u>
  - Dispersal and alignment of nanotubes in polymers
  - Develop methods to characterize the morphology of the percolation networks they form, and how these determine the electrical properties of the composite
- <u>Accomplishments</u>:
  - Nanotube networks were imaged for the first time *inside* polymers using a new *electric field-induced contrast* SEM technique. Thin films spun on custom electrodes to study alignment techniques and current transport.
  - A generalized model is being developed to model conduction of nanotube networks within polymers (with Vincent Meunier, ORNL)
  - Voltage contrast imaging and electron-beam induced current imaging were used to visualize which nanotubes are participating in conduction
  - Electrophoretic alignment techniques are being developed to align SWNT *inside* polymers to electrodes - *investigating large area techniques*
- <u>Applications:</u>
  - Organic LED and PV devices (with Prof. B. Hu, UT)
  - Plastic electronics
  - Nanotube-polymer large-area lighting concepts

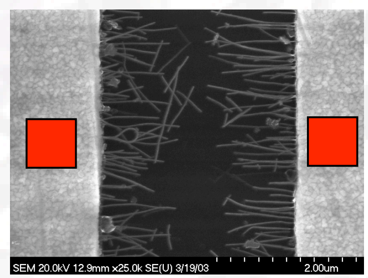




Conductive SWNT networks in polymers - model and reality (between electrodes) in 2D

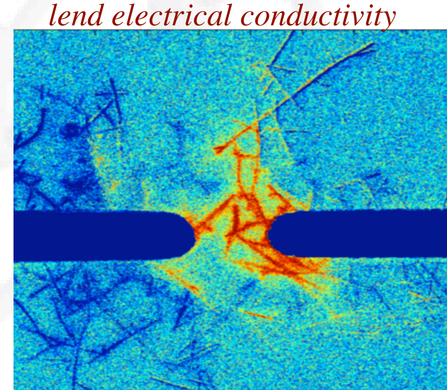


Voltage contrast images of SWNT networks in polymers across biased electrodes as viewed in an SEM



Electrophoretic alignment of SWNT in PMMA

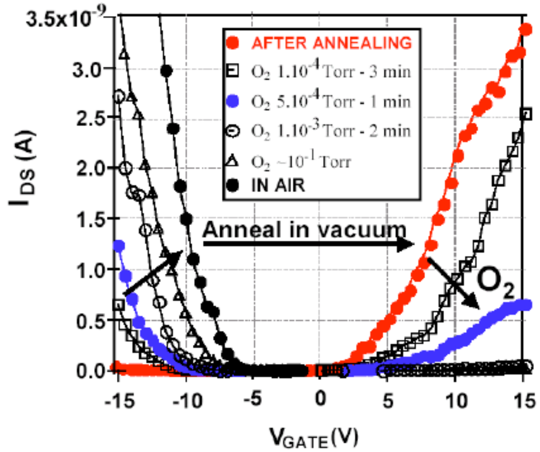
Nanotubes inside polymers lend electrical conductivity



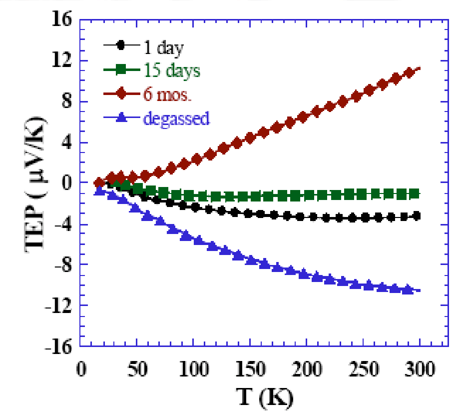
CNMS 2003-058: A. Rao (Clemson Univ.)
Isolated Doped SWNTs for Nanoelectronic Devices

- **Inadvertent doping (air or chemical exposure) of SWNTs can reverse their electronic properties**
  - **n-type to p-type**
  - **thermopower**
- **This limits their long term performance**

- **Irreversible doping of individual SWNT (with substitutional N or B) will be explored**
  - **How will they be synthesized?**
  - **How can doped SWNTs be characterized?**



I-V trace of annealed CNTFET exhibits n-type characteristics which switches to p-type when exposed to ambient conditions



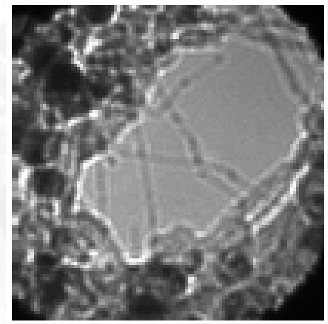
Evolution of TEP for as-prepared MWNT films on quartz under exposure to room air

CNMS 2003-058: A. Rao (Clemson Univ.)

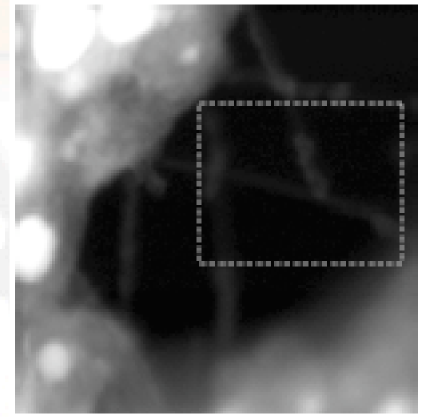
Isolated Doped SWNTs for Nanoelectronic Devices

- **Two synthesis approaches will be explored:**
  - **Laser vaporization - of B and C mixed targets with catalyst**
  - **Chemical vapor deposition combined with Laser Vaporization of B targets**

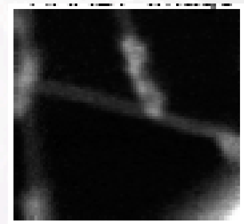
- **Z-STEM imaging and EELS applied to probe B distribution and bonding in SWNTs**



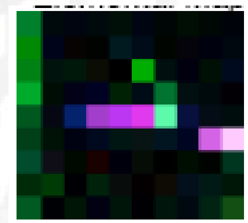
Lo-res TEM-like image



HAADF image: Brightness ~ Z

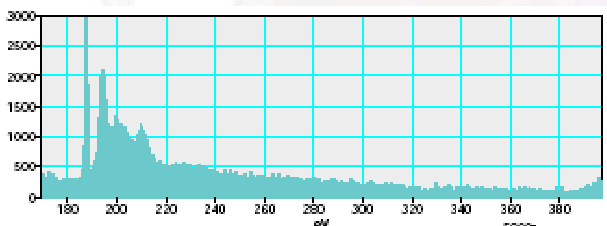


HAADF Image

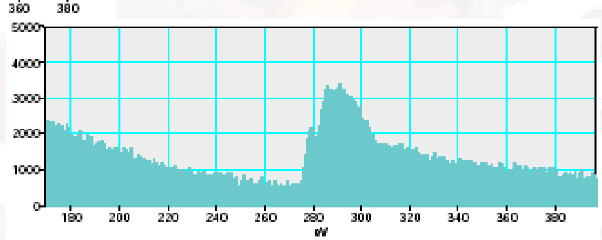


Elemental Map

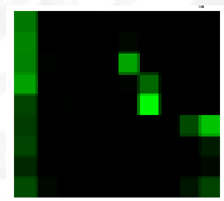
Colorized:
C: Green
B: Blue
N: Red



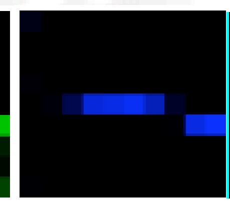
B and N regions



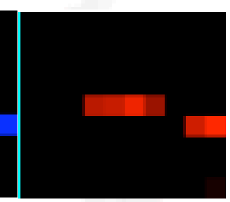
C-like bonding



Carbon Map



Boron Map



Nitrogen Map

Conclusion

- Controlling/understanding synthesis using in situ diagnostics
- Developing a variety of novel nanomaterial synthesis, processing, characterization tools
- Working with users on one of a kind experiments at the forefront of research